EUROPIUM ACTIVATED CESIUM BROMIDE PHOSPHOR AND RADIATION IMAGE STORAGE SHEET

5

FIELD OF THE INVENTION

The present invention relates to an europium acti-
vated cesium bromide phosphor and a radiation image stor-
age sheet utilizing the phosphor.

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BACKGROUND OF THE INVENTION

As a method replacing a conventional radiography, a
radiation image recording and reproducing method utiliz-
15 ing a stimulable phosphor was proposed and has been prac-
tically employed. The method employs a radiation image
storage sheet comprising a support and a stimulable phos-
phor layer (i.e., stimulable phosphor sheet), and com-
prises the steps of causing the stimulable phosphor to
20 absorb radiation energy having passed through an object
or having radiated from an object; sequentially exciting
the stimulable phosphor with an electromagnetic wave such
as visible light or infrared rays (hereinafter referred
to as "stimulating rays") to release the radiation energy
25 stored in the phosphor as light emission (i.e., stimu-
lated emission); photoelectrically detecting the emitted
light to obtain electric signals; and reproducing the
radiation image of the object as a visible image from the
electric signals. The storage sheet thus treated is sub-
30 jected to a step for erasing a radiation image remaining
therein, and then stored for the next recording and re-
producing procedure. Thus, the radiation image storage
sheet can be repeatedly employed.

The stimulable phosphor emits stimulated emission
35 when excited with stimulating rays after having been ex-
posed to a radiation, and a practically used one gives a

stimulated emission in the wavelength region of 300 to 500 nm when irradiated with stimulating rays in the wavelength region of 400 to 900 nm. A typical example of the stimulable phosphor conventionally used in a radiation

5　image storage sheet is an alkali halide phosphor.

For example, Japanese Patent Publication Nos. 7-84588 and 7-84589 disclose CsX and RbX (X: halogen) phosphors. These publications, however, give any information about neither defects of the halogen atom and an amount

10　of Eu^{2+} activator in the phosphor nor the valency of the activating element, particularly, valency of europium (Eu).

The radiation image storage sheet has a basic structure comprising a support and a stimulable phosphor layer

15　provided thereon. If the phosphor layer is self-supporting, the support may be omitted. In general, a transparent protective film of polymer material is placed on the free surface (i.e., surface not facing the support) of the phosphor layer.

20　The phosphor layer usually comprises a binder and stimulable phosphor particles dispersed therein, but it may consist of agglomerated phosphor without binder. The phosphor layer containing no binder can be formed by deposition process or firing process. Further, the phos-

25　phor layer comprising agglomerated phosphor soaked with a polymer is also known. In any of these phosphor layers, the stimulable phosphor emits stimulated emission when excited with stimulating rays after having been exposed to a radiation such as X-ray. The radiation having

30　passed through an object or radiated from an object is absorbed by the phosphor layer of the storage sheet in proportion to the applied radiation dose, and accordingly a radiation image of the object is produced in the storage sheet in the from of a radiation energy-stored image.

35　Thus imagewise stored radiation energy can be released as stimulated emission by sequentially irradiating the stor-

age sheet with stimulating rays. The stimulated emission is then photoelectrically detected to give electric signals, so as to reproduce a visible image from the signals.

5   The radiation image recording and reproducing method (i.e., radiation image forming method) is very advantageous as described above, and it is desired for the radiation image storage sheet employed in the method to have a high sensitivity and give an image of high quality

10. (high sharpness, high graininess).

SUMMARY OF THE INVENTION

It is an object of the present invention to provide

15 an europium activated cesium bromide phosphor which emits an increased amount of stimulated emission.

Further, it is another object of the invention to provide a radiation image storage sheet having high sensitivity.

20 The applicants have studied about the europium activated cesium bromide phosphor, and finally found that the amount of Eu^{2+} (luminescence center) and the number of defects of Br (electron trap) give great effect on the amount of stimulated emission and further found that a

25 ratio of emission strength of Eu^{3+} to Eu^{2+} (Eu^{3+}/Eu^{2+}) preferably is as low as possible to a certain extent.

Accordingly, the present invention resides in an europium activated cesium bromide phosphor having the formula (I):

30   CsBr:xEu   (I)
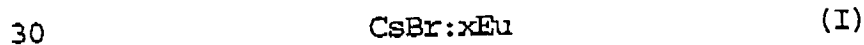
in which x is a number satisfying the condition of $0<x\leq0.2$, wherein a relationship between an emission intensity of Eu^{2+} and a coloring intensity at $F(Br^-)$ center

35 satisfies the following condition:

$$0.2 \leq I_E \times I_F$$

in which I_E and I_F represent the emission intensity and the coloring intensity, respectively.

5   The coefficient x in the formula (I) means the content of Eu in the phosphor. Since the components slightly change during the firing step of the process for preparing the phosphor, the component ratio of raw materials of the phosphor before the firing step often differs from

10   that in the produced phosphor.

In this specification, the term 'emission intensity (I_E) of Eu^{2+}' means a maximum spontaneous emission intensity emitted by Eu^{2+} in the phosphor. The value of I_E is normalized by a maximum emission intensity of a reference

15   phosphor $(SrCaBa)_5(PO_4)_3Cl:Eu^{2+}$ [NP-105 (trade name), Nichia Chemicals Co., Ltd.], which emits luminescence in the same wavelength region, as the phosphor of the invention. Accordingly, I_E is a relative value of the maximum instant emission intensity from Eu^{2+} provided that the

20   emission intensity of $(SrCaBa)_5(PO_4)_3Cl:Eu^{2+}$ is set at 100.

The term 'coloring intensity (I_F) at $F(Br^-)$ center' is represented by $-\log(I_a/I_o)$ in which I_o represents an intensity of light scattered by the phosphor before exposed to X-rays and I_a represents an intensity of light

25   scattered by the phosphor after exposed to a sufficient amount of X-rays. The value I_F corresponds to the number of defects present in Br.

The present invention also resides in an europium activated cesium bromide phosphor having the formula (I):

30

CsBr:xEu   (I)

in which x is a number satisfying the condition of $0<x\leq0.2$, wherein a ratio of Eu^{3+} to Eu^{2+} contained in the

35   phosphor in terms of emission intensity satisfies the following condition:

$$5 \times 10^{-5} \leq Eu^{3+}/Eu^{2+} \leq 0.1.$$

It is preferred that the ratio satisfies the condition of $1 \times 10^{-4} \leq Eu^{3+}/Eu^{2+} \leq 1 \times 10^{-2}$.

In the europium activated cesium bromide phosphor of the invention, the emission intensity of Eu^{2+} can be determined by measuring a peak strength of spontaneous emission at approx. 450 nm which emits upon irradiation with a light at a wavelength of 346 nm, while the emission intensity of Eu^{3+} can be determined by measuring a peak strength of spontaneous emission at approx. 595 nm which emits upon irradiation with a light at a wavelength of 394 nm.

The europium activated cesium bromide phosphor of invention preferably is in the form of prismatic crystals.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 shows an emission spectrum from Eu^{2+} in CsBr:0.01Eu phosphor of the invention.

Figure 2 shows a relationship between the coloring intensity at $F(Br^-)$ center and the period of time for exposing CsBr:0.01Eu phosphor to X-rays.

Figure 3 shows a relationship between $I_B \times I_F$ and the amount of stimulated emission.

Figure 4 shows an emission spectrum from Eu^{3+} in CsBr:0.01Eu phosphor of the invention.

Figure 5 shows a relationship between the ratio of emission strength (Eu^{3+}/Eu^{2+}) and the amount of stimulated emission.

DETAILED DESCRIPTION OF THE INVENTION

The europium activated cesium bromide phosphor of the invention can be prepared, for example, in the following manner.

In the first place, cesium bromide and europium bromide are prepared as starting materials. Then, the starting materials are well mixed under solid phase by means of various known mixing apparatuses. For improving

5 the characteristics of stimulated emission, metal oxides such as aluminum oxide, silicon dioxide and zirconium dioxide may be added, if desired, to the mixture in an amount of not more than 0.5 mol., per one of the phosphor material. In addition, halides of alkali metals (e.g.,

10 Li, Na, K, Rb), alkaline earth metals (e.g., Mg, Ca, Sr) and/or trivalent metals (e.g., Y, La, Al, Ga, In, Tl) may be added in an amount of not more than 0.5 mol., per one of the phosphor material.

The mixture is then placed in a heat-resistance con-

15 tainer such as an alumina crucible or a quartz boat, and fired in an electric furnace. The temperature for the firing is preferably in the range of 100 to 620°C, and particularly preferred is nearly 525°C. As the firing atmosphere, a nitrogen gas atmosphere, a nitrogen gas

20 atmosphere containing a small amount of oxygen gas or hydrogen gas, or an oxygen gas atmosphere can be employed. Preferred is a nitrogen gas atmosphere or a nitrogen gas atmosphere containing a small amount of oxygen gas. The firing period is determined upon various condi-

25 tions such as the amount of the mixture charged in the container, the firing temperature and the temperature at which the product is taken out of the furnace, but generally in the range of 0.1 to 10 hours, preferably 0.5 to 5 hours.

30 The produced phosphor can be subjected to known treatments such as pulverizing and sieving, if needed.

Thus, the europium activated cesium bromide phosphor which is a stimulable phosphor and has the following formula (I) can be prepared.

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$$CsBr:xEu \qquad\qquad (I)$$
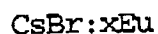
in which x is a number satisfying the condition of $0 < x \leq 0.2$.

The activator of the europium activated cesium bromide phosphor of the invention is in the form of Eu^{2+} or Eu^{3+}. In the process for preparation of the phosphor, all the starting materials for the activator are not always incorporated as the activating components of the resultant phosphor. Accordingly, in the phosphor prepared under some conditions, the total amount of Eu is slightly different from the amount of Eu^{2+}. The amount of stimulated emission generally increases in proportion to the amount of luminescence center Eu^{2+} in the phosphor up to a certain limit. In the present invention, the amount of Eu^{2+} is determined by a maximum instant emission intensity of Eu^{2+} in the phosphor. The maximum instant emission intensity of Eu^{2+} (I_E) is normalized by that of a reference phosphor which emits luminescence in the same wavelength region [$(SrCaBa)_5(PO_4)_3Cl:Eu^{2+}$, NP-105 (trade name), Nichia Chemicals Co., Ltd. in a sufficient concentration to absorb exciting rays].

Accordingly, the value I_E is a relative value of the maximum instant emission intensity from Eu^{2+} provided that the maximum emission intensity of $(SrCaBa)_5(PO_4)_3Cl:Eu^{2+}$ is set at 100. The higher the value I_E is, the more amount of Eu^{2+} the phosphor is present.

The amount of stimulated emission of the above phosphor also increases in proportion to the number of defects of electron trap Br. In the invention, the number of defects of Br is determined by coloring intensity [I_F] at F(Br⁻) center caused by exposure to X-rays. The coloring intensity [I_F] is defined as $-\log(I_a/I_o)$ in which I_o represents an intensity of light scattered by the phosphor before exposed to X-rays and I_a represents an intensity of light scattered by the colored phosphor after exposed to X-rays. The higher the value I_a is (namely, the thicker the phosphor is colored), the more defects of Br

the phosphor are present.

Although both the amount of Eu^{2+} and the number of Br defects increase the amount of the stimulated emission, the emission can not be sufficiently enhanced only by one of them. Only when both of them are enough present in the phosphor, the amount of the stimulated emission remarkably increases. In fact, the europium activated cesium bromide phosphor of the invention releases the stimulated emission in a remarkably increased amount when the emission intensity I_E of Eu^{2+} and the coloring intensity I_F satisfy the condition of $0.2 \leq I_E \times I_F$. It is preferred that these values satisfy the condition of $0.5 \leq I_E \times I_F \leq 30.0$, and more preferably satisfy the condition of $10.0 \leq I_E \times I_F \leq 15.0$.

The radiation image storage sheet of the invention has a phosphor layer (or film) comprising an europium activated cesium bromide phosphor of the formula (I).

The phosphor layer is usually formed by a vapor-phase deposition method, and hence usually comprises the phosphor in the form of prismatic crystals. The phosphor layer may further contain other stimulable phosphors. Furthermore, the storage sheet of the invention may have another phosphor layer containing other phosphors such as a phosphor absorbing radiation energy to emit visible or ultraviolet light. As an example for preparation of the radiation image storage sheet of the invention, the process for preparing the storage sheet having a phosphor layer formed on a support by a vapor-phase deposition method is described below.

The support employed in the invention can be optionally selected from those employed in the conventional radiation image storage sheets. Preferred examples of the support include sheets of quartz, glass, metals (e.g., aluminum, iron, tin, chromium) and resins (e.g., aramide). For improving sensitivity or image quality (such as sharpness or graininess) of the storage sheet,

it is known to provide a light-reflecting layer containing light-reflecting material such as titanium dioxide or a light-absorbing layer containing light-absorbing material such as carbon black. These auxiliary layers may be

5 optionally formed on the support. Further, for improving the sharpness of the resultant radiation image, fine hollows may be formed on the phosphor layer-side surface of the support or on the phosphor layer-side surface of the auxiliary layer such as an adhesive layer, the light-re-

10 flecting layer or the light-absorbing layer, if provided.

In the case where the phosphor layer is formed by a vacuum deposition method, firstly the support is placed in a container of vacuum deposition apparatus. After the container is evacuated to approx. 1.33×10^{-4} Pa, the sti-

15 mulable phosphor is heated and evaporated by a resistance heating method or an electron beam method to be deposited on the support until a phosphor layer having the desired thickness is formed. The vacuum deposition may be repeated for several times, and different phosphors may be

20 co-deposited using two or more resistance heaters or electron beams. Further, it is also possible to form the phosphor layer on the support simultaneously with preparing the phosphor from the starting materials. The support (or a protective layer formed on the support) may be

25 cooled or heated, while the phosphor is deposited on it. After the vacuum deposition is complete, the formed (deposited) phosphor layer may be subjected to a heating (anile) treatment. The treatment is carried out, for example, at a temperature of 50 to 600°C for a few hours

30 under nitrogen gas (which may contain a small amount of oxygen or hydrogen gas) atmosphere.

If the electron beam method is adopted, firstly the aforementioned stimulable phosphor or a mixture of its starting materials is pressed to prepare a tablet as an

35 evaporation source. The pressure is determined according to character and a state of the phosphor, and is general-

ly in the range of 800 to 1,000 kg/cm^2. The phosphor or the materials may be heated at a temperature of 30 to 200°C during the pressing. The formed tablet is prefer-ably degassed after pressed. Thus prepared tablet has a relative density of 80 to 98%, preferably 90 to 96%. From the surface of the tablet, the phosphor can be uni-formly evaporated.

The tablet of the stimulable phosphor (evaporation source) and the support (on which the phosphor is depos-ited) are placed in a container of vacuum deposition apparatus, and the container is evacuated to approx. 1,33x10^{-2} to 1.33x10^{-4} Pa. While that vacuum is kept, an inert gas such as Ar or Ne gas may be introduced. The distance between the evaporation source and the support is set in the range of 5 to 150 cm. An electron beam is generated by an electron gun at an accelerating voltage of 1.5 to 5.0 kV (preferably 2.0 to 4.0 kV), and applied on the source. By exposing to the electron beam, the stimulable phosphor is evaporated, and deposited on the surface of the support. The rate of deposition of phos-phor (namely, the deposition rate) is generally in the range of 1 to 1,000 μm/min., preferably in the range of 1 to 100 μm/min. After the vacuum deposition is complete, the formed phosphor layer may be subjected to a heating treatment. The treatment is carried out, for example, at a temperature of 50 to 600°C for 1 to 3 hours under nitro-gen gas (which may contain a small amount of oxygen or hydrogen gas) atmosphere.

In the case that the phosphor layer is formed by a sputtering method, firstly the support is placed in a container of sputtering apparatus. After the container is once evacuated to approx. 1.33x10^{-4} Pa, an inert gas for sputtering (e.g., Ar or Ne gas) is introduced to ap-prox. 0.133 Pa. The stimulable phosphor is set as a target, and the gas is ionized by discharging. The phos-phor is sputtered and deposited on the support until a

phosphor layer having the desired thickness is formed. The sputtering may be repeated for several times, and different phosphors may be simultaneously or sequentially sputtered from two or more targets to form two or more phosphor layers. Further, it is also possible to form the phosphor layer on the support simultaneously with preparing the phosphor by sputtering the starting materials simultaneously or sequentially. If needed, O_2 or H_2 gas may be introduced into the apparatus to perform reactive sputtering. The support (or a protective layer formed on the support) may be cooled or heated while the sputtering is performed. After the sputtering is completed, the formed (deposited) phosphor layer may be subjected to a heating (anile) treatment.

Thus, the phosphor layer comprising prismatic crystals of the stimulable phosphor growing along the thickness direction can be obtained. This phosphor layer does not contain any binder and consists of the stimulable phosphor alone. In the phosphor layer, there are cracks among the prismatic crystals of the stimulable phosphor. The thickness of the phosphor layer can be selected according to characteristics of the storage sheet and conditions of the vapor-phase deposition method, but is generally in the range of 100 μm to 1 mm (preferably, 200 to 700 μm). It is not necessary to form the phosphor layer directly on the support from the vapor phase. For example, the phosphor layer may be prepared by the steps of forming a phosphor film on a temporary support (e.g., glass plate, metal plate, plastic sheet) from the vapor phase, peeling off the formed sheet, and then providing the film onto a desired support with adhesive.

The phosphor layer may comprise a binder resin and the phosphor particles dispersed therein. In that phosphor layer, other stimulable phosphors and/or additives such as colorant may be incorporated. The phosphor layer can be formed, for example, in the following known man-

ner. First, the stimulable phosphor and a binder are added in an appropriate organic solvent, and mixed well to prepare a coating dispersion in which the phosphor particles are uniformly dispersed in an organic binder resin solution. The binder employed in the invention can be optionally selected from those known and employed in the conventional radiation image storage sheets. The ratio between the binder and the phosphor in the coating liquid is generally in the range of 1:1 to 1:100 (binder:phosphor, by weight), preferably in the range 1:8 to 1:40 (by weight). Thus prepared coating liquid is homogeneously applied on a support by known coating means (such as doctor blade, roll coater, and knife coater).

The formed layer is then dried to form a stimulable phosphor layer. The thickness of the phosphor layer is designed according to the characteristics of the phosphor, the desired characteristics of the storage sheet and the mixing ratio of binder and phosphor, but generally in the range of 20 μm to 1 mm, preferably 50 μm to 500 μm. The phosphor layer may be formed by other steps, namely, coating the coating dispersion on a temporary support, drying the coated dispersion to form a phosphor film, peeling off the phosphor film, and then providing the phosphor film with adhesive or by pressing onto the support.

On the phosphor layer, the protective film is preferably provided so as to avoid deterioration of the sheet and/or to improve handling in conveying the sheet. The protective film preferably is transparent so as not to affect transmission of the stimulating rays and the stimulated emission. Further, the protective film preferably has enough chemical stability, enough moisture resistance and enough physical strength to protect the storage sheet from chemical deterioration or physical shock. The protective film can be formed, for example, by the aforementioned vacuum deposition method such as the electron beam

method. The conditions of the method are, for example, a vacuum degree of 1.33×10^{-2} to 1.33×10^{-4} Pa, a distance between the evaporation source and the support in the range of 5 to 150 cm, an accelerating voltage of 1.5 to 5.0 kV

5 and a deposition rate of approx. 1 μm/min.

Otherwise, the protective film can be formed by coating the phosphor layer with a solution containing a transparent polymer material (e.g., cellulose derivatives, polymethyl methacrylate) dissolved in an appropri-

10 ate solvent, or by fixing a beforehand prepared transparent film (e.g., glass plate, a film of polymer material such as polyethylene terephthalate) on the phosphor layer with adhesion. The protective film may be formed by coating a solution of organic solvent-soluble fluorocar-

15 bon resin dispersing powder of perfluoro-olefin resin or silicone resin. The thickness of the protective film generally is in the range of 0.1 to 20 μm.

Thus, the radiation image storage sheet of the invention can be obtained. The storage sheet of the inven-

20 tion include various known variations. For example, for improving the sharpness of the resultant image, at least one of the aforementioned layers may be colored with a colorant which does not absorb the stimulated emission but the stimulating rays.

25 The present invention is further described by the following examples.

[Example 1] Preparation of CsBr:0.01Eu phosphor

15 g (0.07 mol.) of cesium bromide and 0.2761 g

30 (7.0×10^{-4} mol.) of europium bromide were weighed and mixed in a mixer. The obtained mixture was charged in a quartz container, and placed in an electric furnace. The furnace was then evacuated (first evacuation) and filled with nitrogen gas of atmospheric pressure. After the

35 mixture was fired at 525°C for 1 hour, the furnace was evacuated again for 5 minutes (second evacuation) and

then filled with oxygen gas of 133 Pa. Further, nitrogen gas was introduced to the furnace until the inner pressure reached atmospheric pressure. After the mixture in thus treated furnace was again fired at the same temperature for 1 hour, the furnace was evacuated. The product in the furnace was cooled to room temperature. The cooled product was taken out of the furnace, and pulverized in a mortar to prepare the desired europium activated cesium bromide phosphor particles.

[Example 2] Preparation of CsBr:0.01Eu phosphor

The procedure of Example 1 was repeated except that the furnace after the second evacuation was filled with oxygen gas of not 133 Pa but 266 Pa, to prepare europium activated cesium bromide phosphor particles.

[Example 3] Preparation of CsBr:0.01Eu phosphor

The procedure of Example 1 was repeated except that the mixture was fired for 2 hours under nitrogen gas atmosphere without performing the second evacuation, to prepare europium activated cesium bromide phosphor particles.

[Example 4] Preparation of CsBr:0.01Eu phosphor

The procedure of Example 1 was repeated except that the furnace after the second evacuation was filled with oxygen gas of not 133 Pa but 399 Pa, to prepare europium activated cesium bromide phosphor particles.

[Example 5] Preparation of CsBr:0.01Eu phosphor

The procedure of Example 1 was repeated except that the furnace after the first evacuation was filled with hydrogen gas of 39.9 Pa, nitrogen gas was further introduced into the furnace until the inner pressure reached atmospheric pressure, and then the mixture was fired at 500°C for 2 hours. Thus, europium activated cesium bro-

mide phosphor particles were prepared.

[Example 6] Preparation of CsBr:0.01Eu phosphor

The procedure of Example 1 was repeated except that

5   the furnace after the second evacuation was filled with
oxygen gas of not 133 Pa but 1330 Pa, to prepare europium
activated cesium bromide phosphor particles.

[Comparison Ex. 1] Preparation of CsBr:0.0001Eu phosphor

10   15 g (0.07 mol) of cesium bromide and 0.0028 g
$(7.0 \times 10^{-6}$ mol) of europium bromide were weighed out and
mixed in a mixer. The obtained mixture was charged in a
quartz container, and placed in an electric furnace. The
furnace was then evacuated (first evacuation) and filled

15   with nitrogen gas of atmospheric pressure. After the
mixture was fired at 550°C for 2 hours, the furnace was
evacuated. The product in the vacuous furnace was cooled
to room temperature. The cooled product was taken out of
the furnace, and pulverized by means of a mortar to pre-

20   pare the titled europium activated cesium bromide phos-
phor particles.

[Evaluation of Produced Phosphor]

With respect to each of the stimulable phosphors

25   prepared above, the emission intensity (I_E) from Eu^{2+}, the
coloring intensity (I_F) centered at $F(Br^-)$ and the amount
of stimulated emission were measured in the following
manners to evaluate the phosphor.

(1) Measurement of emission intensity (I_E) from Eu^{2+}

30   The phosphor particles were packed in a holder hav-
ing a quartz window, and the instant emission from Eu^{2+} in
the phosphor was measured by means of a spectrofluoro-
meter (F-4500, Hitachi, Ltd.). The conditions of the
measurement were as follows:

35   voltage of photomultiplier: 400 V
slit width on excitation side: 2.5 nm

slit width on emission side: 2.5 nm

scanning speed: 60 nm/min.

wavelength of exciting rays: 346 nm.

5   From the measured emission spectrum, the maximum intensity at approx. 450 nm was obtained.

Next, a reference phosphor $(SrCaBa)_5(PO_4)_3Cl:Eu^{2+}$ [NP-105 (trade name), Nichia Chemicals Co., Ltd.], which emits a luminescence in the same wavelength region as the sample phosphor, was packed in the same holder. The reference phosphor was exposed to exciting rays of 370 nm, and the spontaneous emission spectrum was measured in the same manner. From the measured emission spectrum, the maximum intensity of the reference phosphor at approx. 450 nm was obtained.

The maximum intensity of the sample phosphor was normalized and expressed in terms of a relative value provided that the maximum intensity of the reference phosphor was set at 100. Thus, the emission intensity (I_E) from Eu^{2+} was obtained.

(2) Measurement of coloring intensity (I_F) at $F(Br^-)$ center

The phosphor particles (200 mg) were uniformly packed in a black cylindrical holder (aperture: 10 mm, depth: 250 μm). A very weak probe rays were applied onto the surface of the phosphor cropped out at the aperture, and light scattered from the phosphor was collected by a photomultiplier (R-1848, Hamamatsu Photonics Co., Ltd.) through an optical filter (O-50, Hoya Corporation) to measure the intensity (I_o) of light scattered by the phosphor.

Next, the phosphor was exposed to X-rays (40 kVp, 30 mA) for 20 minutes, and light (I_a) scattered from the phosphor was measured in the same manner. From the measured I_o and I_a, $-\log(I_a/I_o)$ was calculated to obtain the

coloring intensity (I_F) centered at F(Br$^-$).

(3) Ratio of emission strength (Eu^{3+}/Eu^{2+})

A spectrofluorometer (F-4500, Hitachi, Ltd.) was
first subjected to the following spectral correction
procedures.

1) Correction of exciting wavelength

Rhodamine B which was approximately constant in its
quantitative efficiency at different wavelengths was in-
corporated into a quartz cell. In the spectrofluoro-
meter, an exciting spectrum at an emission wavelength of
640 nm was measured to obtain an correction coefficient
of exciting wavelength for make the spectrum strengths at
different wavelengths. The measurement was performed
under the following conditions:

voltage of photomultiplier: 400 V
slit width on excitation side: 5.0 nm
slit width on emission side: 20 nm
scanning speed: 60 nm/min.

2) Correction of emission wavelength

A glass diffusion element which is approximately
constant in its scattering strength at different wave-
lengths is subjected to measurement of scattering spec-
trum in the spectrofluorometer, to obtain an correction
coefficient of emission wavelength for make the scatter-
ing spectrum strengths at different wavelengths. The
measurement was performed under the following conditions:

voltage of photomultiplier: 400 V
slit width on excitation side: 5.0 nm
slit width on emission side: 20 nm
scanning speed: 60 nm/min.

3) Ratio of emission strength (Eu^{3+}/Eu^{2+})

The phosphor particles were packed in a holder hav-
ing a quartz window, and the instant emission from Eu^{2+} in

the phosphor was measured by means of the spectrofluoro-
meter. The conditions of the measurement were as fol-
lows:

5

  voltage of photomultiplier: 400 V
  slit width on excitation side: 2.5 nm
  slit width on emission side: 2.5 nm
  scanning speed: 60 nm/min.
  wavelength of exciting rays: 346 nm.

  From the measured emission spectrum, the maximum

10 intensity at approx. 450 nm was obtained.

  Next, the phosphor was exposed to exciting rays of
394 nm under the same conditions, and the spontaneous
emission spectrum was measured at approx. 595 nm in the
same manner.

15   The strength of exciting light at each wavelength
and the strength of emission light at each wavelength
were corrected using the above-obtained correction
coefficiencies. Then, a ratio of the emission strength
of Eu^{3+} to the emission strength of Eu^{2+} was calculated to

20 give the desired Eu^{3+}/Eu^{2+}.

  (4) Stimulated emission

  The phosphor particles (200 mg) were uniformly
packed in a black cylindrical holder (aperture: 10 mm,

25 depth: 250 μm). In a dark room, X-rays (80 kVp) from an
X-ray generator (MG164, Phillips) were applied in the
amount of 100 mR through an Al filter of 3 mm thick onto
the surface of the phosphor cropped out at the aperture.
After the phosphor was left for 20 seconds, light (660

30 nm, 4.3 J/m²) from a semiconductor laser (ML-1016R,
Mitsubishi Electric Co.) was evenly applied onto the
phosphor surface to cause stimulated emission. The stim-
ulated emission was collected by a photomultiplier (R-
1848, Hamamatshu Photonics Co., Ltd.) through an optical

35 filter (B-410, Hoya Corporation) to measure the amount of
stimulated emission.

With respect to CsBr:0.01Eu phosphor, the emission spectrum from Eu^{2+} in the phosphor and the relationship between the coloring intensity (I_P) at F(Br⁻) center and the exposure to X-rays are shown in Figures 1 and 2, respectively. The results of the above evaluations are set forth in Figures 3 and 5 and Tables 1 to 3.

An emission spectrum from Eu^{2+} in CsBr:0.01Eu phosphor of the invention is shown in Fig. 1.

A relationship between the coloring intensity centered at F(Br⁻) and the period of time for exposing CsBr:0.01Eu phosphor to X-rays is shown in Fig. 2.

A relationship between the value of $I_B \times I_P$ and the amount of stimulated emission is shown in Fig. 3.

An emission spectrum from Eu^{3+} in CsBr:0.01Eu phosphor of the invention is shown in Fig. 4.

A relationship between the ratio of emission strength (Eu^{3+}/Eu^{2+}) and the amount of stimulated emission is shown in Fig. 5.

Table 1

	phosphor	firing condition	
		temperature	atmosphere
Ex. 1	CsBr:0.01Eu	525°C	N_2(O_2:133 Pa)
Ex. 2	CsBr:0.01Eu	525°C	N_2(O_2:266 Pa)
Ex. 3	CsBr:0.01Eu	525°C	N_2
Ex. 4	CsBr:0.01Eu	525°C	N_2(O_2:399 Pa)
Ex. 5	CsBr:0.01Eu	500°C	N_2(H_2:39.9 Pa)
Ex. 6	CsBr:0.01Eu	525°C	N_2(O_2:1330 Pa)
C.Ex.1	CsBr:0.0001Eu	550°C	N_2

Table 2

	I_E	I_F	$I_E \times I_F$	stimulated emission
Ex. 1	56	0.1799	10.0	37.7
Ex. 2	51	0.2639	13.5	45.2
Ex. 3	55	0.2362	13.0	47.6
Ex. 4	47	0.2245	10.6	43.1
Ex. 5	11	0.1679	1.9	16.9
Ex. 6	2	0.2635	0.6	12.6
C.Ex.1	2	0.1237	0.1	1.5

It is evident from Figure 3 and Table 2 that the
europium activated cesium bromide phosphors of the inven-
tion (Examples 1 to 6), which showed products of the
emission intensity (I_E) from Eu^{2+} and the coloring inten-
sity (I_F) at F(Br$^-$) center in the range of more than 0.2,
emitted much more amount of stimulated emission than the
phosphor for comparison (Comparison example 1). In par-
ticular, the phosphors showing $I_E \times I_F$ of more than 10.0
(Examples 1 to 4) emitted very much amounts of stimulated
emission. The value of $I_E \times I_F$ can be controlled by proper-
ly setting the temperature and the atmosphere of firing
procedure, as shown in Figure 1.

Table 3

	Emission Strength Eu^{2+}	Eu^{3+}	Ratio Eu^{3+}/Eu^{2+}	stimulated emission
Ex. 1	56	0.010	1.9x10^{-4}	37.7
Ex. 2	51	0.014	2.9x10^{-4}	45.2
Ex. 3	55	0.022	4.0x10^{-4}	47.6
Ex. 4	47	0.029	6.1x10^{-4}	43.1
Ex. 5	11	0.044	3.9x10^{-3}	16.9
Ex. 6	2	0.073	3.1x10^{-2}	12.6
C.Ex.1	2	2.6x10^{-5}	1.3x10^{-5}	1.5

It is evident from Figure 5 and Table 3, the europium activated cesium bromide phosphors of the invention which show the Eu^{3+}/Eu^{2+} ratios in the range of 5x10^{-5} to 0.1 (Examples 1 to 6) give an apparently increased amount of stimulated emission, as compared with the phosphor of Comparison example 1. Particularly, when the Eu^{3+}/Eu^{2+} ratio is in the range of 1x10^{-4} to 1x10^{-2}, the stimulated emission is given in a prominently large amount.

The europium activated cesium bromide phosphors of the invention which have the specific Eu^{3+}/Eu^{2+} ratio can be prepared by adjusting the firing temperature and the firing atmosphere.

[Example 7]
Preparation of Radiation Image Storage Sheet
(1) Preparation of evaporation source
100 g (0.47 mol) of cesium bromide and 3.18404 g (4.7x10^{-3} mol) of europium bromide were mixed and pulverized in a mortar, and further mixed and stirred in a stirring shaker for 15 minutes. The obtained mixture was

placed in an electric furnace. The furnace was then evacuated (first evacuation) for 3 minutes, and filled with nitrogen gas of atmospheric pressure. After the mixture was fired at 525°C for 2 hours, the furnace was

5   evacuated again for 15 minutes. The product in the vacuous furnace was cooled to room temperature. The obtained europium activated cesium bromide phosphor (CsBr:0.01Eu) was pulverized in a mortar, and pressed by 950 kg/cm² to prepare a tablet as an evaporation source. The tablet

10 was degassed at 150°C for 2 hours.

(2) Formation of phosphor film

An aluminum sheet was washed with methyl ethyl ketone, cleaned with ultraviolet rays and ozone, and dried

15 in a clean booth. Independently, a glass sheet and a quartz sheet were washed with an alkali, and dried in the clean booth. These sheets were used as supports. Each support was placed in a container of vacuum evaporation apparatus, and the prepared evaporation source was set at

20 a predetermined position. After the container is evacuated to 4.0×10^{-4} Pa, an electron beam (28 mA) generated by an electron gun at an accelerating voltage of 4.0 kV was applied on the source for 16 minutes. By exposing to the electron beam, the stimulable phosphor was evaporated and

25 deposited on the surfaces of the supports at the deposition rate of 25 μm/min. After the evaporation was complete, air was introduced into the apparatus until the inner pressure reached atmospheric pressure. The supports were then taken out of the apparatus. On the sur-

30 face of each sheet, a phosphor film (thickness: 400 μm) in which prismatic crystals (width: 30 μm, length: 400 μm) of the phosphor thickly stood together in large numbers was thus formed.

Thus, a radiation image storage sheet comprising a

35 support and a phosphor layer according to the invention was produced.